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## Description

The invention relates to a ceramic composition adapted to form a coating on a metal, said coating being obtained by applying the composition in aqueous slurry. The invention also relates to a method for preparing and applying the composition, the use thereof, and an internal combustion engine exhaust pipe coated with layers of the composition.

## Background

In present-day technology, there is a growing need for efficient and formable insulating materials that must have high temperature resistance, excellent thermal insulating power, excellent resistance to thermal shocks, and excellent resistance to chemical corrosion. Such insulating materials are especially attractive to the metal working industry which uses large quantities of sheet-metal, steel and aluminium.

The interest in such materials is especially pronounced in the motor industry (for coating exhaust pipes and engine parts) and in the offshore and ship-building industries (for coatings protecting against fire, corrosion and erosion). Furthermore, these materials are used in combustion plants and processes and in household appliances (kitchen ranges, refrigerators). Above all, however, the motor industry is interested in these materials since motor-cars equipped with catalysts require an appropriate insulation of the exhaust pipe.

It is known from DE-OS 2,751,918 to provide motor-car exhaust pipes with an internal heat-insulating coating consisting of a ceramic slurry with an embedded metal lattice, the interstices of which are filled with the slurry which contains for example sodium silicate, alumina, binder and water. EP-A 101,911 discloses a ceramic coating, in particular for the inner side of an exhaust pipe, said coating containing, besides conventional components, lithium aluminium silicate. US-A 4 248 752 discloses a composition for heat-insulating coatings, said composition comprising ceramic fibres, finely divided silica, an adhesion agent and, optionally, hollow spheres of plastic or ceramic material. It merely appears that the material may be used for insulating furnace walls and furnace parts, and no mention is made of motor-car parts or exhaust pipes.

From GB-A 1.117.950 a ceramic composition for use in bonding an insulating blanket of refractory fibres to a metal surface is known, which composition contains a potassium silicate, barium carbonate and possibly alumina powder. This cement composition thus merely acts as an adhering agent between the insulating blanket and the metal surface, though it is mentioned that a small part of finely chopped ceramic fibres can be included in the cement composition in order to increase the thermal shock resistance of the cement. No mention is made of use in exhaust pipes, the only use stated being on large areas and on steel plates.

## The invention

There has now been developed a heat-insulating composition adapted to form a coating on metal, said composition having excellent characteristics in respect of adhesion, insulating power and resistance to temperature, corrosion and thermal shocks. The composition contains ceramic fibres, an inorganic filler, a silica binder material and hollow microparticles in specific proportions and, furthermore, potassium silicate and, optionally, a surface-active agent. In addition, the composition contains water as a carrier material. The composition according to the invention thus comprises, in % by weight:

- 10 - 50% of potassium silicate
  - 10 - 50% of colloidal silica
  - 5 - 40% of inorganic filler
  - 1 - 25% of ceramic fibres
  - 2 - 40% of water
  - 2 - 20% of hollow microparticles
  - 0 - 5% of surface active agent
- A composition suitable for most applications is, in % by weight:
- 20 - 35% of potassium silicate
  - 20 - 35% of colloidal silica
  - 10 - 25% of inorganic filler
  - 4 - 15% of  $\text{Al}_2\text{O}_3\text{-SiO}_2$  fibres
  - 8 - 25% of water
  - 2 - 8% of hollow microparticles
  - 0 - 5% of surface active agent

The introduction of potassium silicate into the composition in order to obtain binding and sintering properties constitutes an essential improvement of the temperature resistance because potassium silicate can withstand higher temperatures than the sodium silicates previously used in similar contexts. In addition, this component is far cheaper than the lithium aluminium silicates previously used for such applications. The preferred silicate is potassium water glass, and a suitable molar ratio  $K_2O:SiO_2$  is about 3.3. A higher molar ratio imparts a higher viscosity to the slurry.

Besides its binding function, the silica material also serves as a thickener for the slurried composition, and also as a sintering agent. The preferred form is finely divided silica, preferably in colloidal form. Colloidal silica is a product containing about 50%  $SiO_2$  and 50% by weight of water.

The inorganic filler improves the insulating power of the layer and affects the properties of the slurry in respect of viscosity, dispersing power and homogeneity. Suitable inorganic fillers may be, for example, talc or zirconia.

The ceramic fibres usually consist of a mineral material, and as a rule use is made of fibres having a high length-to-width ratio. The fibres preferably consist of an  $Al_2O_3-SiO_2$  material capable of withstanding temperatures between  $900^\circ C$  and  $1600^\circ C$ . The melting point of the fibres varies with the ratio of  $Al_2O_3$  to  $SiO_2$ .

The statement regarding the water content of the composition relates to the amount added in order to obtain a suitable slurry, and it should be noted that the potassium silicate contains bonded water, and that the silica binder, especially the colloidal silica, contains product water.

Hollow microparticles are incorporated in order to improve the consistency of the slurry and to simplify the drying process by making the system more porous for water removal and for imparting to the finished layer a low heat conductivity. The increased content of air because of the hollow microbodies considerably increases the insulating ability of the coating. The microparticles are hollow filler bodies which usually are spherical. With some types of metal, a small amount of a surface active agent may be incorporated in the composition in order to obtain improved rheological properties regarding the flowability of the slurry on the substrate upon application thereto.

The composition according to the invention is primarily intended to be applied to the inner side of an exhaust pipe. On present-day motor-cars equipped with catalysts, the exhaust pipe is heat-insulated between the engine and the catalyst to quickly reach the ignition temperature of the catalyst. As a rule, the insulation was applied to the outside of the exhaust pipe, because the corrosive atmosphere within the pipe in particular and also the great variations in temperature causes difficulties. However, if the insulating layer is applied to the inner side of the exhaust pipe, the exhaust temperature will rise more quickly, by about 10-20%, in that the exhaust pipe as such is not heated, and the heat is instead conducted directly to the catalyst. On the other hand, it was found difficult to impart to the internal layer the requisite characteristics.

A closely related composition is disclosed in US-A 4,248,752 which, however, makes no mention of its application to exhaust pipes and the specific problems encountered in that connection. The prior art composition was tested in a number of comparison tests together with the composition according to the invention, and it was found that the prior art composition has a higher corrosion tendency than the present composition, primarily because it has a higher pH value, i.e.  $pH = 11$ , whereas the composition according to the invention has  $pH = 9$ . Furthermore, the finished coating comprising the prior art composition is fairly soft, presumably because it comprises an adhesion agent, whereas the coating according to the invention is hard.

In a preferred embodiment of the invention, the composition comprises, in % by weight:

25 - 30% of potassium water glass

25 - 30% of colloidal silica

15 - 20% of inorganic filler

5 - 10% of  $Al_2O_3-SiO_2$  fibres

2 - 5% of hollow microspheres

10 - 20% of water

The composition according to the invention is produced by 1) mixing potassium silicate with ceramic fibres; 2) adding silica binder under continuous agitation; 3) adding the inorganic filler and water and continuing agitation until a homogeneous mixture is obtained; and 4) adding microparticles under careful agitation.

When the composition according to the invention is to be used as a heat-insulating coating on an internal combustion engine exhaust pipe, it is applied in viscous water-slurried form by so-called "pouring through" technique, i.e. the slurry is poured through the pipe to form a coating, dried at  $50-150^\circ C$  for 0.5-3 hours and at  $150-300^\circ C$  for 0.5-2 hours, optionally followed by one or more further drying cycles, whereupon the procedure is repeated from 2 to 5 times, preferably 3 times. Each separate layer may obtain

a thickness of about 0.5 mm, and a total layer thickness of 1-1.5 mm is preferred.

For some applications with extreme temperature conditions, exhaust port liners are used, and a ceramic composition according to the invention can be applied by casting-in into the interspaces of the pipe to form a so-called sandwich structure. Immersion technique is used for applying the desired layer which is dried as indicated above before a further layer, if any, is applied. For such cast-in coating, a very high temperature resistance is more important than the mechanical strength characteristics.

#### Example 1

From a ceramic composition according to the invention a slurry was prepared which comprised

| Components            | Contents (g) | M.P.      |
|-----------------------|--------------|-----------|
| Potassium water glass | 26.3         |           |
| Silica sol 50/80 (1)  | 26.3         | 1710 °C   |
| Talc                  | 18.5         | > 1400 °C |
| Ceramic fibre (2)     | 7.9          | 1760 °C   |
| Hollow spheres        | 2.6          | > 600 °C  |
| Water                 | 18.4         |           |
|                       | 100.0        |           |

(1) colloidal silica, concentration/surface area (conc. = 50% SiO<sub>2</sub> in H<sub>2</sub>O; surface area = 80 m<sup>2</sup>/g).

(2) ceramic fibre having a heat conductivity of less than 1.0 W/K7m.

The slurry contained 55% solid matter and was prepared as follows.

Potassium water glass was mixed with fibre until the fibre was wet. Silica sol 50/80 was added under continuous agitation. Talc and water were added, and agitation continued until a homogeneous mixture was obtained. Hollow spheres were added under careful agitation.

The composition is suitable for coating the inner side of a motor-car exhaust pipe, and the maximum working temperature is assumed to amount to 800 °C. The coating as such can withstand about 1000 °C.

The coating thus prepared was applied to the inner surface of a test pipe by so-called "pouring through" technique. Only one layer was applied which was dried at 70-100-150 °C for 2 hours and then at 200-300 °C for 1 hour. The resulting layer had a thickness of more than 0.5 mm.

The mechanical properties of the layer were as follows

|                |   |
|----------------|---|
| Vibration test | 10x10 <sup>6</sup> cycles at 25 Hz                          |
| Crush strength | 50-100 kg/cm <sup>2</sup>                                   |
| Hardness       | 1-3 mm indentation by 5 mm ball pressed at a load of 120 kg |

It appears from these test results that the layer made from the composition according to the invention is highly resistant to mechanical stress.

Example 2

From a ceramic composition according to the invention a slurry was prepared which comprised

| Components            | Contents (g) | M.P.      |
|-----------------------|--------------|-----------|
| Potassium water glass | 27.8         |           |
| Silica sol 50/80 (1)  | 27.8         | 1710 °C   |
| Talc                  | 16.7         | > 1400 °C |
| Ceramic fibre (2)     | 11.1         | 1760 °C   |
| Metaspheres 100 (3)   | 5.61         | 1350 °C   |
| Water                 | 11.0         |           |
|                       | 100.0        |           |

(1) colloidal silica, concentration/surface area (conc. = 50% SiO<sub>2</sub> in H<sub>2</sub>O; surface area = 80 m<sup>2</sup>/g).

(2) ceramic fibre having a heat conductivity of less than 1.0 W/K7m.

(3) hollow bodies of especially high-melting glass where 100 is a measure of the particle size distribution ( $\mu$ ).

The slurry contained about 58% solid matter and 52% upon dilution with an additional 100 g water. The slurry was prepared in the same manner as in Example 1.

The composition thus prepared is suitable for applications that must withstand temperatures of at least 1400 °C (the temperature of molten iron), especially for applications using casting-in technique, but also for other high temperature uses. The melting points of all components are extremely high.

The composition was applied to an exhaust port liner in the following manner. The liner was immersed in the slurry and conducted to a drier where it was dried as follows: 50-70-100 °C/45 min, 100-120-140 °C/45 min, 150-170 °C/30 min, 200 °C/10 min. After cooling to room temperature, a second layer was applied in analogous manner and dried as follows: 50-70-100-120-150 °C/2 hours, 150-200-250-300 °C/2 hours. The resulting coating had a thickness of about 1-1.5 mm.

In this instance, the mechanical strength was not tested since a cast-in material in a sandwich structure is better protected against mechanical stress. In this instance, the extremely high temperature resistance is very important.

It has thus been found that the ceramic composition according to the present invention is capable of establishing on metal a coating which has excellent mechanical strength characteristics and an excellent temperature resistance.

**Claims**

1. A composition for forming a heat-insulating ceramic coating on a metal, **characterised** in that the composition comprises, in % by weight:

10 - 50% of potassium silicate

10 - 50% of colloidal silica

5 - 40% of inorganic filler

1 - 25% of ceramic fibres

2 - 40% of water

2 - 20% of hollow microparticles

0 - 5% of surface active agent.

2. A composition as claimed in claim 1, **characterised** in that the potassium silicate is potassium water glass.

3. A composition as claimed in claim 1, **characterised** in that the ceramic fibres consist of an Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> material.

4. A composition as claimed in claim 1, **characterised** in that the inorganic filler consists of talc or zirconia.

5. A composition as claimed in any one of claims 1-4, **characterised** in that it comprises, in % by weight:
  - 20 - 35% of potassium silicate
  - 20 - 35% of colloidal silica
  - 10 - 25% of inorganic filler
  - 4 - 15% of  $\text{Al}_2\text{O}_3\text{-SiO}_2$  fibres
  - 8 - 25% of water
  - 2 - 8% of hollow microparticles
  - 0 - 5% of surface active agent.
6. A method for preparing a composition as claimed in claim 1, **characterised** by
  - 1) mixing potassium silicate with ceramic fibres;
  - 2) adding colloidal silica under continuous agitation;
  - 3) adding inorganic filler and water and continuing agitation until a homogeneous mixture is obtained;
  - and
  - 4) adding hollow microparticles under careful agitation.
7. Use of a composition as claimed in claim 1, for forming a heat-insulating coating on a metal.
8. The use as claimed in claim 7, **characterised** in that said heat-insulating coating is applied to an exhaust pipe by pouring the composition in viscous water-slurried form through the pipe, or by immersing the pipe in the slurry, whereupon the pipe is dried at 50-200 °C for 0.25-3 hours and at 100-300 °C for 0.5-2 hours, optionally followed by one or more further drying cycles, whereupon the coating procedure is optionally repeated from 1 to 5 times until the desired layer thickness is obtained.
9. Exhaust pipe of an internal combustion engine, **characterised** in that it is provided with a coating consisting of one or more layers of a composition as claimed in claim 1.

#### Patentansprüche

1. Zusammensetzung zur Ausbildung einer wärmeisolierenden Keramikbeschichtung auf einem Metall, dadurch gekennzeichnet, daß die Zusammensetzung in Gew.-% umfaßt:
  - 10 - 50 % Kaliumsilikat,
  - 10 - 50 % kolloidales Siliciumdioxid,
  - 5 - 40 % anorganischen Füllstoff,
  - 1 - 25 % keramische Fasern,
  - 2 - 40 % Wasser
  - 2 - 20 % Mikroteilchen mit Hohlraum,
  - 0 - 5 % oberflächenaktives Mittel.
2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Kaliumsilikat Kaliumwasserglas ist.
3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die keramischen Fasern aus einem  $\text{Al}_2\text{O}_3\text{-SiO}_2$ -Material bestehen.
4. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der anorganische Füllstoff als Talk oder Zirkoniumdioxid besteht.
5. Zusammensetzung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß sie in Gew.-% umfaßt:
  - 20 - 35 % Kaliumsilikat,
  - 20 - 35 % kolloidales Siliciumdioxid,
  - 10 - 25 % anorganischen Füllstoff,
  - 4 - 15 %  $\text{Al}_2\text{O}_3\text{-SiO}_2$ -Fasern,
  - 8 - 25 % Wasser,
  - 2 - 8 % Mikroteilchen mit Hohlraum,
  - 0 - 5 % oberflächenaktives Mittel.

6. Verfahren zur Herstellung einer Zusammensetzung nach Anspruch 1, gekennzeichnet durch
  - 1) Mischen von Kaliumsilikat mit keramischen Fasern;
  - 2) Zugabe von kolloidalem Siliciumdioxid unter kontinuierlichem Rühren;
  - 3) Zugabe von anorganischem Füllstoff und Wasser, wobei das Rühren solange fortgesetzt wird bis ein homogenes Gemisch erhalten wird; und
  - 4) Zugabe von Mikroteilchen mit Hohlraum unter vorsichtigem Rühren.
7. Verwendung einer Zusammensetzung nach Anspruch 1 zur Ausbildung einer wärmeisolierenden Beschichtung auf einem Metall.
8. Verwendung nach Anspruch 7, dadurch gekennzeichnet, daß man die wärmeisolierende Beschichtung auf ein Auspuffrohr durch Gießen der Zusammensetzung in viskoser, wasseraufgeschlammter Form durch das Rohr, oder durch Eintauchen des Rohrs in die Aufschlämmung aufbringt, nachfolgend das Rohr 0,25 bis 3 Stunden bei 50 bis 200 °C und 0,5 bis 2 Stunden bei 100 bis 300 °C trocknet, gegebenenfalls gefolgt von einem oder mehreren weiteren Trocknungszyklen, und man danach das Beschichtungsverfahren gegebenenfalls 1 bis 5 mal wiederholt, bis die gewünschte Schichtdicke erhalten wird.
9. Auspuffrohr eines Verbrennungsmotors, dadurch gekennzeichnet, daß es mit einer Beschichtung versehen ist, die aus einer oder mehreren Schichten einer Zusammensetzung gemäß Anspruch 1 besteht.

#### Revendications

1. Composition pour former un revêtement céramique isolant thermique sur un métal, caractérisée en ce que la composition comprend, en pourcentage pondéral:
  - 10 à 50% de silicate de potassium
  - 10 à 50% de silice colloïdale
  - 5 à 40% d'une charge minérale.
  - 1 à 25% de fibres céramiques
  - 2 à 40% d'eau
  - 2 à 20% de microparticules creuses
  - 0 à 5% d'agent tensio-actif
2. Composition selon la revendication 1, caractérisée en ce que le silicate de potassium est un verre soluble potassique.
3. Composition selon la revendication 1, caractérisée en ce que les fibres céramiques se composent d'un matériau de  $Al_2O_3-SiO_2$ .
4. Composition selon la revendication 1, caractérisée en ce que la charge minérale se compose de talc ou de zircon.
5. Composition selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle comprend, en pourcentage pondéral:
  - 20 à 35% de silicate de potassium
  - 20 à 35% de silice colloïdale
  - 10 à 25% de charge minérale
  - 4 à 15% de fibres  $Al_2O_3-SiO_2$
  - 8 à 25% d'eau
  - 2 à 8% de microparticules creuses
  - 0 à 5% d'agent tensio-actif.
6. Procédé pour préparer une composition selon la revendication 1, caractérisé par les opérations consistant:
  - 1) à mélanger du silicate de potassium avec des fibres céramiques;
  - 2) à ajouter de la silice colloïdale sous agitation continue;

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- 3) à ajouter une charge minérale et de l'eau sous agitation continue jusqu'à obtention d'un mélange homogène; et
- 4) à ajouter des microparticules creuses sous agitation soignée.

- 5 7. Utilisation d'une composition selon la revendication 1, pour former un revêtement isolant thermique sur un métal.
- 8. Utilisation selon la revendication 7, caractérisée en ce que ledit revêtement isolant thermique est appliqué sur un tuyau d'échappement en versant la composition sous forme d'une suspension aqueuse visqueuse à travers le tuyau, ou en immergeant le tuyau dans la suspension, ce sur quoi on sèche le tuyau à 50 à 200 °C pendant 0,25 à 3 heures et à 100 - 300 °C pendant 0,5 à 2 heures, éventuellement suivi par un ou plusieurs cycles de séchage supplémentaires, ce sur quoi on répète éventuellement le procédé de revêtement de 1 à 5 fois jusqu'à obtention de l'épaisseur de couche souhaitée.
- 15 9. Tuyau d'échappement d'un moteur à combustion interne, caractérisé en ce qu'il est équipé d'un revêtement se composant d'une ou de plusieurs couches d'une composition selon la revendication 1.

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